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Distributed hydrogen production from ethanol in a microfuel processor: Issues and challenges

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ABSTRACT

In the contemporary era of looming energy crunch, hydrogen fuel, obtained from ethanol, is a potentially strong contender as an energy carrier, based on a renewable source. Moreover, acknowledging the critical importance of distributed power devices and systems on one hand and the importance of microscale engineering on the other, we envisage developing an ethanol-based distributed hydrogen production device of the order of 1 kW using steam reforming of ethanol (SRE). In this paper, the key issues related to this microscale distributed hydrogen production strategy are discussed in view of its potential application for polymer electrolyte membrane (PEM) fuel cells. The design challenges and issues related to various essential micro-devices, viz., the pre-heater, fuel reformer, water gas shift (WGS) reactor, carbon monoxide preferential oxidation (CO PrOX), required for efficient production of H_2 with very low concentration of CO contamination, are discussed. Various production schemes are carefully evaluated for the purpose. Need for integration of micro-devices is emphasized to obtain a compact fuel processor system.

Contents

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Nomenclature

D	Diameter (m)
g	Acceleration due to gravity (m/s^2)
h	Heat transfer coefficient (W/m^2 K)
ΔH	Enthalpy of formation (J/mol)
K_{eq}	Equilibrium reaction constant
L_c	Laplace constant (m)
P	Pressure (Pa)
q''	Heat flux (W/m^2)
T	Temperature (°C or K)

Symbols

ρ	Density (kg/m^3)
σ	Surface tension (N/m)

Subscripts

b	Bubble point
h	Hydraulic
l	Liquid
mix	Binary mixture
v	Vapor
w	Wall

Abbreviations

ATR	Auto-thermal reforming
HT	High temperature
LT	Low temperature
PO	Partial oxidation
PrOX	Preferential oxidation
SR	Steam reforming
WGS	Water gas shift reaction

1. Introduction

Unless definitive measures are implemented soon enough, the world is heading towards a severe and prolonged energy crunch in the not-too-distant future. In the historical background of the de-carbonization pattern of primary fuel usage, hydrogen is emerging as a natural choice as a more secure and cleaner energy carrier [1]. Hydrogen can be produced from a variety of sources including fossil fuels (coal, natural gas, LPG, gasoline, diesel, methane, propane, wind, solar, methanol, ethanol, bio-fuel, etc.) but to decrease the dependence on fossil fuels, fully or partially, current situation strongly demands that hydrogen should be produced from a renewable source. In this context, ethanol/bio-ethanol is a promising biomass-derived liquid fuel for hydrogen production [2,3]. Hydrogen can be produced from a variety of feed stocks using a variety of methods; a brief review of these methods is presented below, before we take up the issues related to the ethanol route for hydrogen production.

2. Methods of hydrogen production

Methods of hydrogen production can be broadly classified as (a) thermo-chemical, (b) electrolysis of water, (c) photochemical, and (d) biological.

2.1. Thermo-chemical processes

2.1.1. Steam reforming (SR)

Steam reforming refers to the reaction between steam and a hydrocarbon, typically producing hydrogen in the process. Use of natural gas or naphtha as a raw material is an industrial process. Typical reactions are highly endothermic in nature. Depending on the purity of hydrogen required, WGS and PrOX reactors are also appended to this process. The industrial catalyst used for this reaction is Ni/α-Al_2O_3. While the steam/carbon ratio required for this reaction is 2, generally 2.5–3.0 molar ratios are used to avoid coke formation. Since this is an endothermic and kinetically controlled reaction, temperatures in the range of 1073–1173 K are used to obtain desirable reaction rates. Main disadvantages of this process include the formation of CO_2, a global warming gas, as a byproduct, and the use of non-renewable natural gas feedstock.

2.1.2. Partial oxidation (PO)

Partial oxidation (PO) is another industrially used process to produce H_2 or syngas from hydrocarbons, with following stoichiometric equation:

$$C_xH_y + 0.5xO_2 \rightarrow xCO + 0.5yH_2 \quad (1)$$

PO compares better than SR as it is not only non-catalytic but also does not require external thermal energy input. The process requires temperatures of 1400–1700 K and pressures ranging from 30 to 100 bar. Pure oxygen is used instead of air to avoid the N_2 separation step. Catalyst may be used to appreciably reduce the reaction temperature. The primary disadvantage of this process as compared to SR is low hydrogen yield.

2.1.3. Auto-thermal reforming (ATR)

Combining the features of SR and PO, ATR has been developed, utilizing both steam and oxygen along with the feedstock [4]. The oxygen to fuel ratio is sub-stoichiometric and can be altered to adjust the process temperature. The hydrocarbon feed stock first reacts with oxygen and the released heat is used for steam reforming reaction. This takes place on the reforming catalyst placed after the burner in the reactor. In this process, the hydrogen yield is more than that in PO, but less than that in SR. Moreover, this process does not require any external heat to be supplied.

2.1.4. Pyrolysis

Hydrocarbons, when heated to ~1600 °C, are converted to pure carbon and H_2, with no other significant side products. This, therefore, is quite a viable process for H_2 production; of course, till fossil fuel-based feedstock is economically available.

2.2. Electrolysis

Electrolysis of water, i.e. applying electricity to split it, is a process by which almost 100% pure hydrogen can be obtained. This is the next commonly used industrial method, after steam reforming of methane. At present, conventional alkaline electrolyte-based electrolysis is economical, only if cheap electricity is available. Research is primarily focused on the feasibility of using solid oxide steam electrolyzer, PEM electrolyzer, etc. [5–10].

2.3. Photochemical decomposition

Photo-catalytic splitting of water, using nano-sized TiO_2 catalyst, is a potentially feasible process for production of hydrogen from water. Very low process efficiency is the main hurdle. This low efficiency is attributed to (i) rapid recombination of photo generated electron/hole pair and (ii) backward reaction

[11,12]. Some sacrificial reagents such as S^{2-}/SO_3^{2-} [11], Ce^{4+}/Ce^{3+} [13] and IO_3^-/I^- [14] and electron donors such as methanol [15] are under study for enhancing production. Catalyst modification techniques, such as noble metal loading [16,17], ion doping [18], dye sensitization [19] and metal ion implantation are also being studied [20].

2.4. Bio-hydrogen

Biological hydrogen production is carried out by several methods including direct and indirect bio-photolysis, photo-fermentation and dark-fermentation, the latter being the most efficient [21]. Dark-fermentation involves the use of anaerobic bacteria (*Clostridium pasteurianum*, *C. butyricum*, and *C. beijerinkii*) grown in the dark on carbohydrate rich substrates to produce H_2, CO_2 and traces of CH_4, CO, and H_2S. Using *Rhodospirillum rubrum*, H_2 can be produced from WGS reaction when only CO is available [22]. The main disadvantage of this method is the very slow rate of production.

3. Why use ethanol?

All the methods mentioned above have some inherent limitations (such as dependence on fossil fuel, low rates/process efficiency, etc.) which hinder their use for sustainable energy generation, at least at this point of time. In this context, ethanol steam reforming is a viable process for generating energy from biomass-based fuel. Ethanol is a promising future bio-fuel because of its relatively high hydrogen content (on molar basis), non-toxicity, ease of storage and handling safety. Ethanol can be readily produced from renewable feed stocks such as sugar cane, municipal solid waste and agro-waste. Another advantage of using ethanol is that the CO_2 produced during steam reforming reaction is equal to the CO_2 required for biomass growth and thus provides a closed cycle for CO_2 consumption. Therefore, no net pollutants are released into the environment. Primary demerit includes high reforming temperatures (~600 °C).

4. Why use micro-reactors?

During the last two decades, technological developments in micro-manufacturing systems have gained considerable momentum [23]. Miniaturization has become the key word in many advanced as well as traditional industries and is being progressively applied in commercial sectors such as pharmaceutical, medical, military, energy and electronics industries, to name a few. Recently, micro-devices and systems (popularly known as micro-reactors), having their characteristic dimensions typically of the order of few micrometers, have also attracted the interest of chemical process industry because of certain inherent advantages [24–26].

The obvious discerning characteristics of micro-reactors are compact size, light weight, and lower material and energy consumption. Secondly, smaller linear dimensions lead to increased species gradients (momentum flux, concentration, temperature) which are particularly important for chemical reactor processing. This results in rapid heat and mass transport, and short diffusion lengths. Faster system response gives better process control and high product yields. Besides these, the attractive feature of micro-reactors is their high surface to volume ratio compared to conventional chemical reactors. Because of smaller passage size, flow through micro-reactors usually remains laminar. Thus, the heat/mass transfer coefficients become inversely proportional to the channel hydraulic diameter; of course there is increase in corresponding momentum flux transfer, i.e. pressure drop. Nevertheless, overall heat/mass transfer to pressure drop ratio is increased.

The higher heat and mass transfer characteristics of micro heat exchangers are an added advantage for utilizing the full potential of catalysts used, especially during endothermic/exothermic

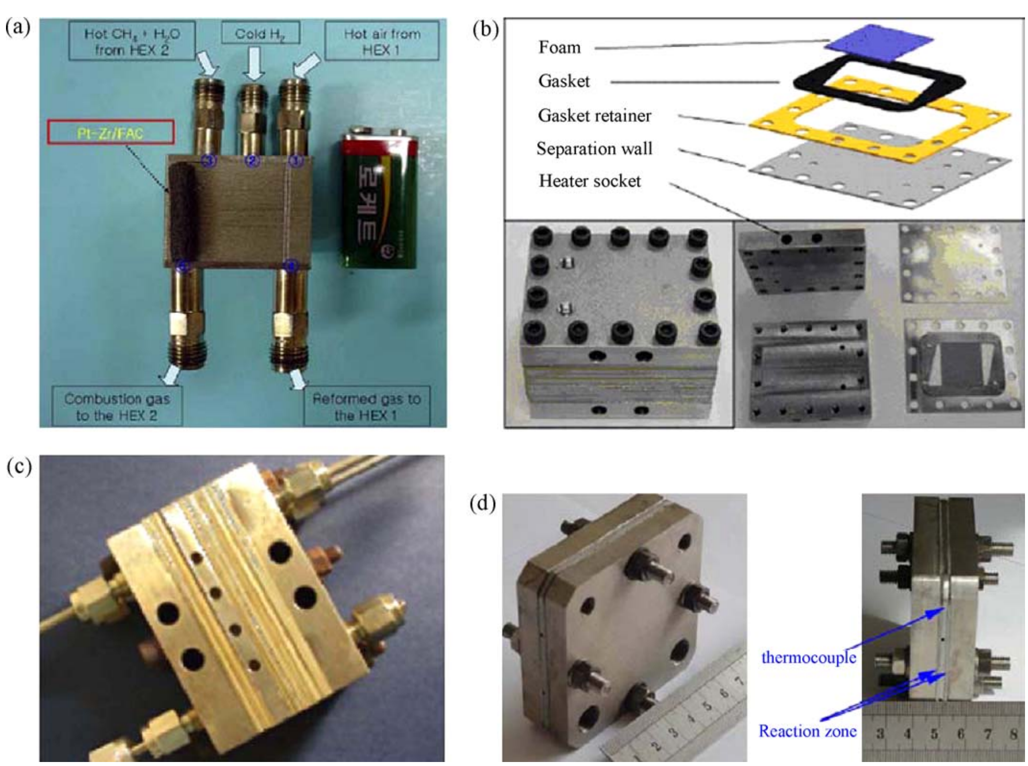


Fig. 1. Various types of micro-reactors [27–30]. Individual array of microchannel plates is stacked together to complete a leak-tight assembly having inlet and outlet manifolds for reactant and products, respectively.

reactions. Thus, local hot-spot formations are avoided because of high heat removal capacity. Secondly, because of higher reaction temperature, catalysis can be utilized effectively, thus requiring a smaller volume. This leads to low operating cost and higher system efficiency. Finally, because of smaller reactants and products inventories, high level of safety is achieved. Fig. 1 shows some examples of types of micro-reactors which have been reported in recent times [27–30].

5. Integrated reactor system for steam reforming of ethanol and CO cleanup

The production of H_2 from ethanol includes the reaction of ethanol with steam, followed by steps to reduce the CO content of the product stream. As shown in Fig. 2, water and ethanol are mixed together and then fed to a pre-heater where flow boiling of the mixture takes place by application of external heat input. The gas-phase mixture is further superheated to the desired reaction temperature. The pre-heated vapor is fed to the reformer, where the mixture reacts to form hydrogen as well as other compounds, such as CO_2, CO and CH_4. As the produced hydrogen is rich in CO ($\sim$10 mol%), a cleanup unit needs to be attached after the reformer. As shown in Fig. 2, three possible routes are being investigated for reducing the CO content in the product stream: (a) membrane separation; where the effluent is passed through a membrane after reforming, which allows only H_2 molecules to pass through it. In this way 99.99% pure hydrogen can be produced [31]. Other two, (b) and (c) i.e., either via CO PrOX or via CO Methanation, are chemical routes in which CO is reduced to ppm levels by WGS followed by either PrOX or selective methanation of CO.

The routes described above involve several thermal and chemical transport processes, i.e. endothermic/exothermic catalytic reactions, flow boiling of liquid mixtures, single-phase and two-phase heat exchange, etc. In contrast to conventional reactor and heat exchanger systems, micro-reactors provide unique

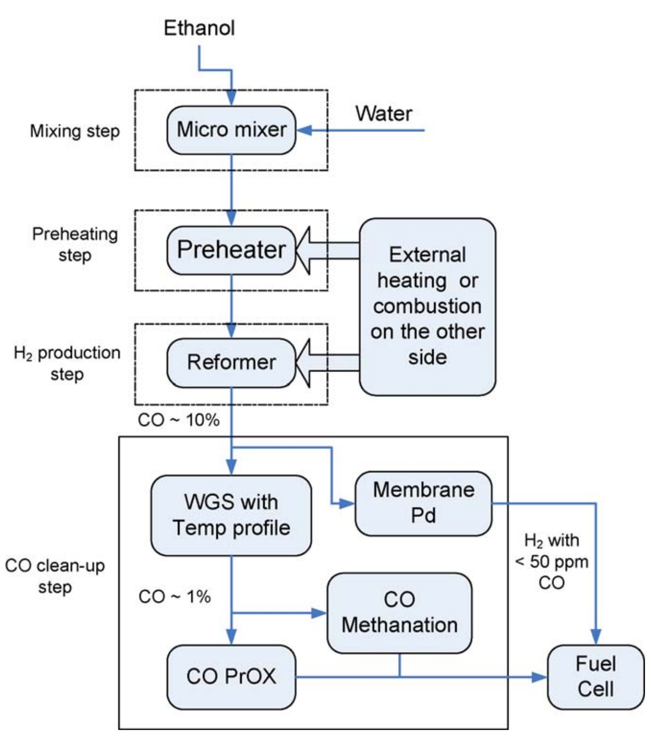


Fig. 2. Schematic of an integrated reactor system for distributed generation of hydrogen from ethanol and water. Four major building units, (i) mixer, (ii) pre-heater, (iii) reformer and (iv) CO cleanup stages are required to develop an integrated reactor system.

features not only in the integration of various thermo-chemical processes described above, but also by meeting the demands of space optimization in distributed systems. Heat resistant materials like Klingersil® can be used to avoid unwanted heat exchange between the devices, while making the overall system compact. In recent times, the relative merit of micro-reactors has been studied by many groups [32–34].

It is envisaged to develop an ethanol-based hydrogen production device of the order of 1 kW using steam reforming of ethanol (SRE) coupled with fundamentals of microscale engineering. Such a system can meet the growing demands of distributed power in emerging economies and developing world.

The stoichiometry of the reaction for maximum hydrogen production by catalytic ethanol steam reforming process is:

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2: \quad \Delta H_{298} = 174\,\text{kJ/mol} \tag{2}$$

The produced hydrogen is made to react with oxygen (or air) to form water and thermal energy:

$$H_2 + 0.5O_2 \rightarrow H_2O + 241.8\,\text{kJ/mol of } H_2O \tag{3}$$

Thus, stoichiometry requires a mixture of 2.4 ml/min of C_2H_5OH and 2.23 ml/min of H_2O for producing 1 kW of thermal energy equivalent. In real-time practice, to avoid coke formation and to enhance the selectivity towards reforming reaction, a steam-rich mixture is desired [35]. Thus, assuming water to ethanol molar ratio of 1:6 (stoichiometry = 1:3), the amount of water required would be 4.5 ml/min. By assuming a W/F_{A0} of 1.00 (W = weight of the catalyst and F_{A0}= molar flow rate of the reactant A (i.e. ethanol), the amount of catalyst required would be $\sim$2.5 g. With this data, if the cross-section area of the microchannel is of the order of $\sim$500 μm^2, the length of reactor is of the order of $\sim$50 mm, catalyst layer thickness of $\sim$30 μm, number of microchannels per reactor plate $\sim$25, the number of reactor plates required works out be about 30.

5.1. Pre-heater design issues

With the advent of micro and meso scale thermo-fluidics and chemical systems, the development of ultra-compact process units such as heat exchangers, micro pumps and turbines and micro thermal systems has become an important research activity area, especially in the distributed power production parlance. The production for mixture feed for the ethanol steam reformer necessitates application of a micro heat exchanger in the upstream location, before the catalytic reactions can commence. The catalytic steam reforming of ethanol for hydrogen production is highly endothermic (ΔH_{673} = 208.4 kJ/mol), which accounts for the requirement of high reforming temperatures usually around $\sim$873 K [36]. A pre-heater, consisting of a phase-change micro heat exchanger and a superheater, are therefore needed to convert the liquid phase reactants (water and ethanol) to superheated gas phase, before entering the micro-reactor. In this background, the fundamental understanding of thermo-hydrodynamics of flow boiling of pure fluids and binary mixtures is a precursor to design the catalytic reformer.

5.1.1. Role of physical properties of liquid mixture

When one or more components are mixed together, the physical properties of the resulting mixture are required to describe the new fluid. In some cases the mixing is ideal, which means that the mixture properties can be obtained by a simple linear mixing law approach using the component concentrations and the pure fluid properties at the same temperature. But in most instances the mixing is not ideal and the heat of mixing, non-ideal variation in viscosity, surface tension, density, etc. must be estimated with more sophisticated methods. Some of the resulting

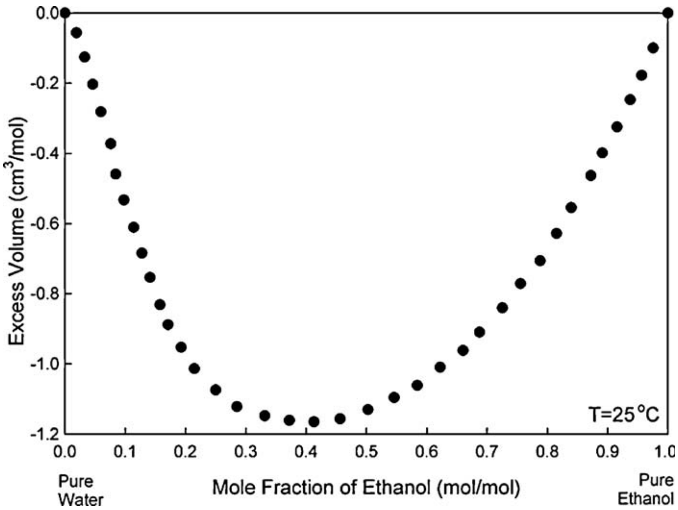


Fig. 3. Excess volume of the ethanol–water mixture; as can be seen there is a reduction of resultant volume when ethanol and water are mixed together.

properties may not lie between those of the pure components. For example, Fig. 3 shows the variation of resulting mixture volume with respect to ethanol concentration [37]. As can be seen, the mixture volume is always lower than the constituent volume of the individual components. For example, mixing equal volumes of ethanol and water result in only 96% of the total initial component volumes. Even very large variations can occur especially with liquid viscosity and latent heat [38]. Information on suitable predictive methods is available in data books, for example, [39].

Physical properties important to boiling and nucleation are contact angle and surface tension. The data for variation of contact angle of binary mixtures with varying concentration of the constituent liquids is not very abundant. Shakir and Thome [40] have compiled some data for binary mixtures and highlighted the non-linear behavior of contact angle with concentration. The addition of relatively small quantities of a second component to water often greatly reduces the surface tension. Fig. 4 shows the changes in bubble point and dew point temperature and in surface tension for the ethanol–water mixture [38]. The reduction in surface tension as the mol fraction of ethanol is increased causes a sharp drop in the superheat required to maintain a given sized embryo in equilibrium.

5.1.2. Flow boiling of pure and binary liquids in mini/microchannels

While flow boiling studies in conventional sized channels dates back to the development of steam boilers and nuclear power reactors, the advent of miniaturization in many engineering systems, for example, emergence of small tonnage unit refrigeration industry, provided the impetus to similar studies in mini/micro geometries. Thus, in recent times, the focus is on experiment, computations, as well as theoretical research on sub-millimeter/micron sized geometries. This is a natural outcome of the quest for higher species transport rates per unit volume of the equipment.

Due to the significant differences of transport phenomena in mini–microsystems as compared to normal sized channels, it is important to define what is meant by the terms 'mini', 'meso' and 'micro', etc.? Unfortunately, an explicit agreement is not established in the literature; there are no clear demarcations of mini/meso/microgeometrical regimes. According to Kandlikar [41], a tentative scheme is as follows:

Conventional channels	$D_h > 3.0$ mm
Minichannels	$3\ \text{mm} \geq D_h \geq 200\ \mu\text{m}$
Microchannels	$200\ \mu\text{m} \geq D_h \geq 10\ \mu\text{m}$

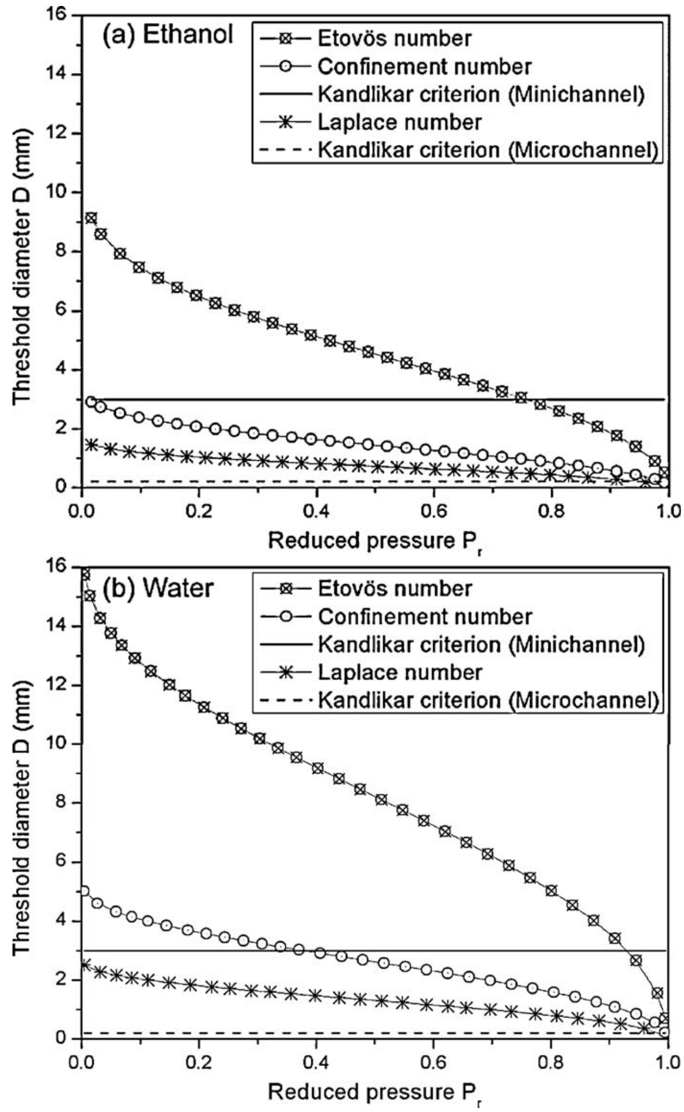


Fig. 4. Variation of threshold diameter as per various definitions, for (a) ethanol and (b) water. There is a large variation in the definitions which specify the acceptable limits wherein microscale effects become predominant.

Other ways of classification could be, for example, based on some relevant non-dimensional numbers of interests, viz., Laplace constant, Confinement number or the Eötvös number (also referred to as the Bond number, Eö = $(\text{Bo})^2$). As defined by Triplett et al. [42] and later by Serizawa et al. [43], if the hydraulic diameter is smaller than the Laplace constant, as defined below, the channel can be considered as a microchannel:

$$L_c = \sqrt{\frac{\sigma}{g \times (\rho_l - \rho_v)}} \tag{4}$$

Kew and Cornwell [44] give another interpretation of the same quantity in terms of the confinement of bubbles in a channel. As will be appreciated, under nucleate flow boiling conditions, microchannels will tend to have elongated Taylor type confined bubbles. Thus, the size of the channel significantly affects the bubble shape and subsequent two-phase species transport. The Confinement number is defined as:

$$\text{Co} = \frac{1}{D_h}\sqrt{\frac{4\sigma}{g \times (\rho_l - \rho_v)}} = \frac{2L_c}{D_h} \tag{5}$$

and can be used to define the transition between microscale effects in boiling systems. Another way to look at the transition is in terms of the applicable wave instability at the fluid–vapor interface, which leads to the definition of the Eötvös number, from the interaction of surface tension and gravity forces, as follows [45]:

$$E\ddot{o} = \left(\frac{2\pi}{D_h}\right)^2 \frac{\sigma}{g \times (\rho_l - \rho_v)} \quad (6)$$

Fig. 4a and b shows the relevant threshold diameters, i.e. transition diameters for considering a channel as 'micro', for ethanol and water, respectively, for the entire range of operating pressures. It is clear that there are considerable differences in the threshold diameters as defined by various criteria. This exemplifies the difficulties in classification of channels based on the comparison of relevant forces; so far, no unified methodology has been suggested. The issue becomes more important when mixtures are the focus of study.

In early 1980s, Tuckerman and Pease [46] first demonstrated experimentally that flow boiling of water through microchannels is capable of removing high heat flux. Shortly after the initial work of Tuckerman and Pease [46], Wu and Little [47] also conducted experiments on flow friction and heat transfer characteristics in microchannels. Since then, there has been an unprecedented upsurge of flow boiling studies through mini/microchannels, using a variety of fluids and passage dimensions. The primary issues in flow boiling of liquids in microchannel geometries which are being addressed, include, amongst others, (a) fundamental physics of nucleation and bubble growth in confined geometries, (b) effect of surface roughness on transport mechanisms, (c) effect of aspect ratio of the flow channels on transport behavior, (d) correct handling of the boundary conditions, (e) additional effects due to surface energy of the tube material, electro-kinetic forces, wettability, etc., (f) flow instability in single channel and parallel channel arrays, and (g) relative importance of nucleate and convective boiling, etc. The current status of the understanding of flow boiling in mini/microchannels has been reviewed from time to time by several authors [45,48–53].

Flow boiling of binary mixtures is inherently more complicated than the pure fluid counterpart due to the fact that (a) there is no unique boiling point temperature for a given operating pressure (as can be seen in Fig. 5), (b) the overall transport mechanism may be limited by the preferential mass transfer process of the less volatile component during phase-change, (c) the composite thermo-physical properties of the mixture may substantially vary from those determined from linear mixing laws, and (d) the bulk liquid contact angle, an important quantity required for understanding boiling mechanism, usually shows highly non-linear behavior with concentration. There are, comparatively, not only few studies available on this topic, most of them are confined to flow boiling studies of binary mixtures of refrigerants [49,54–59].

There are very few studies reported in the literature on flow boiling of binary mixtures in mini/microchannels; prior to 1994, almost no publications exist in open literature [49,60]. Peng and co-workers [60,61] were one of the first to conduct a sequence of experiments to investigate the flow boiling of subcooled binary mixtures (methanol and water) flowing through a variety of microchannels. They investigated the impact of microchannel scale, geometric configuration, liquid velocity, liquid subcooling, and liquid concentration on the flow boiling.

Peng et al. [60] experimentally investigated the subcooled flow boiling heat transfer characteristics of methanol–water binary

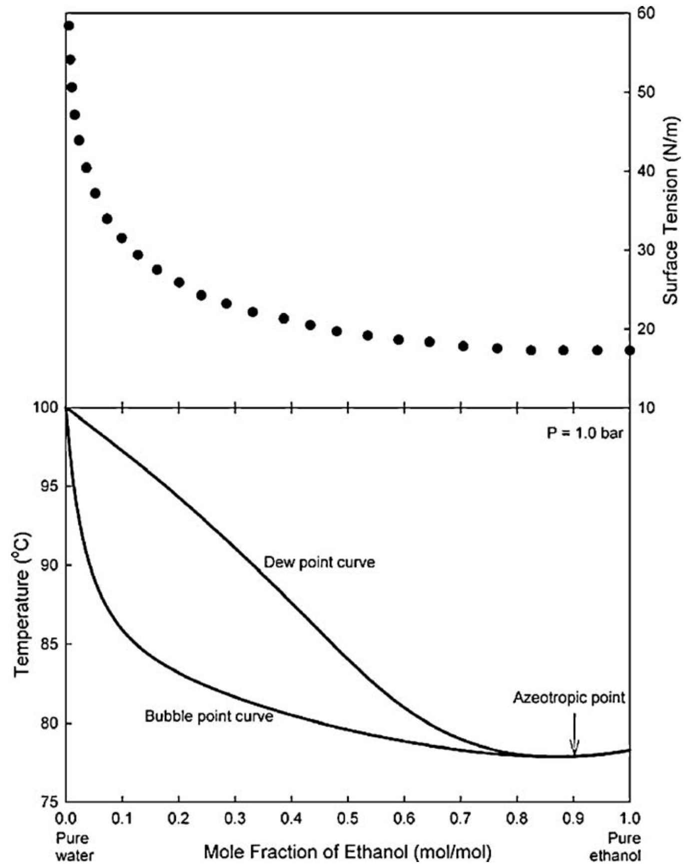


Fig. 5. Bubble point and dew point temperature and corresponding surface tension variation (top graph) of ethanol–water mixture.

mixtures (with mole fractions of the more volatile component of $x = 0$, 5.88, 12.3, 23.2, 36, 51.5, 69.2, 83.5, and 100) in microchannels of size 0.15–0.343 mm. They found that mixtures with small concentrations of the more volatile component augmented the flow boiling heat transfer while those with large concentrations decreased the heat transfer as compared with pure methanol. From this it was concluded that there exists an optimum concentration at which the flow boiling heat transfer reaches a maximum value. These characteristics were found to be affected by both liquid flow velocity and amount of subcooling. The heat transfer coefficient at the onset of flow boiling and in the partial nucleate boiling region was greatly influenced by liquid concentration, microchannel and plate configuration, flow velocity and amount of subcooling. However, microchannel size, flow velocity, subcooling of the mixture, and liquid concentration had no significant effect on the heat transfer coefficient in the fully nucleate boiling regime.

Peng and Peterson [61] also conducted experiments on flow boiling of subcooled binary mixtures of methanol and water in microchannels of hydraulic diameters of 0.133–0.367. They found that hydraulic diameter and aspect ratio significantly affect the fluid flow and heat transfer characteristics. They also found that for smaller mole fractions of the more volatile component (methanol), heat transfer was augmented, and then reached the maximum value at a characteristic mole fraction. The experimental results also indicated that the augmented heat transfer region was extended with increase in mass flow rate through the microchannels.

Recently, Cheng and Mewes [49] have extensively reviewed flow boiling of mixtures in small and mini channels. They have included the investigations during 1996–2005, a majority of which

focus on refrigerant mixtures. They proposed the basic equation for binary mixture to determine the heat transfer coefficient as:

$$h_{\text{mix}} = \frac{q''}{(T_{\text{w}} - T_{\text{b}})} \quad (7)$$

where T_b is the bubble point temperature of the binary mixture and T_w is the wall temperature. For pure fluids, the bubble point temperature equals the saturation temperature.

Peng and Wang [62,63] reviewed experimental and theoretical advances in boiling phase-change and transport phenomena in microchannels and microstructures, including bubble formation, phase transition and the fluid flow and heat transfer characteristics. Their investigations showed that flow boiling heat transfer of pure water, pure methanol, and water–methanol binary mixtures through rectangular and triangular microchannels display some unusual phenomena and characteristics. The experimental results showed that microchannel size, geometric configuration, and mole fraction of water–methanol binary mixtures have a significant impact on the flow boiling, especially for nucleate boiling, and on bubble formation and growth in microchannels. They proposed two new concepts, 'evaporating/boiling space' and 'fictitious boiling', to explain the unusual phase-change transport phenomena, although these concepts were not substantiated with enough evidence.

Though ethanol is being used industrially for a long time, its use for the study of flow boiling in mini/microchannels hardly exists in the literature. Xie et al. [64] experimentally investigated flow and heat transfer characteristics by taking 30% of ethanol–water solution in microchannels. This solution is the most commonly used coolant in the aviation sector. They found that wall temperature has maximum influence on convection heat transfer. No investigation has presented the explicit effect of liquid concentration on the flow boiling heat transfer.

Wu et al. [65] recently conducted experimental study on single-phase flow and heat transfer characteristics of ethanol–water solution in trapezoidal silicon microchannels of hydraulic diameters 141.7–268.6 μm (only single-phase study was reported). Ethanol concentration was varied from 0 to 80% (v/v). They found that the volume concentrations had different effects on the flow friction and heat transfer. While the friction factor was only marginally affected by the change in the volume concentration (within the experimental band of error), there was considerable change in the heat transfer coefficient with the change in the concentration ratio of ethanol and water. The Nusselt number was found to be increasing with the increase of the volume concentration of ethanol. Based on their experimental results, they proposed dimensionless correlations for single-phase flow friction and heat transfer of ethanol–water mixture as a function of cross-sectional geometrical parameters, entrance effect, and volume concentrations.

From the discussions in the above section it is quite clear that very limited number of experimental studies on flow boiling of binary mixtures in mini/microchannels exist. Most existing studies are limited to single-phase flow only. No explicit heat transfer equation and flow pattern studies are available for binary mixtures, especially of ethanol–water mixtures. The state-of-the-art on flow boiling of binary mixtures in microchannels suggests that the following issues need immediate research:

(i) Many more systematic experiments in this area are indeed needed. The effect of component composition on transport behavior is not very clear.
(ii) The interplay between heat transfer and flow patterns is still unclear. Robust visualization of two-phase flow in microchannels continues to pose a challenge.
(iii) A generalized and robust heat transfer model is still not available which takes into account the complex interplay between channel shapes/sizes, component compositions, mass diffusion, flow patterns, etc.
(iv) For practical applications, robust empirical/semi-empirical correlations for two-phase pressure drop and heat transfer are also not readily available.

After the pre-heater (phase-change heat exchanger with superheat), the gaseous feed containing ethanol and water vapor is fed to the fuel reformer. In the next section, we highlight the important chemical engineering aspects of the ethanol reforming unit.

5.2. Steam reforming of ethanol (SRE)

The reactions involved in catalytic steam reforming of ethanol for hydrogen production have been studied extensively over catalysts based on Co, Ni, Ni/Cu as well as noble metals such as Ru, Rh, Pt, and Pd. Cobalt- and copper-based catalysts are more efficient at low temperatures. Rh-based catalysts are more efficient in breaking the C–C bond but are relatively less active for the WGS reaction. Some bimetallic catalysts (Rh–Ni) have been tried to enhance the WGS reaction [66]. Research efforts on development of active, selective and stable catalysts for SRE have increased significantly in the last decade and several reviews have been recently published [35,67–70]. The high temperatures required to obtain reasonable reaction rates increase the coke formation, catalyst sintering and eventual catalyst deactivation. To alleviate this problem, a double layer catalyst system has been proposed. The first layer contains Cu-based catalysts to facilitate dehydrogenation reaction and the second layer contains Ni- or Rh-based catalysts to facilitate C–C bond rupture and to steam reform the acetaldehyde formed on the first catalyst layer [69]. However, at these conditions the chances for side reactions to form methane and carbon monoxide are very high, and thus, the selection of catalyst is critical in this type of configuration.

The heat required for the endothermic reforming reaction can be supplied in several ways: (a) external heat input (by electrical heating), (b) auto-thermal reforming, and (c) combination of combustion/steam reforming reactors with heat exchange between the two, so that heat generated in combustion reaction can be utilized in the steam reforming reaction. For any of the heat supply system mentioned above, micro-devices can be used for efficient heat integration.

Men et al. [71] studied SRE in a microchannel reactor at atmospheric pressure in the temperature range of 400–600 °C, over various noble and non-noble metal catalysts. Wash coating method was used to coat the catalyst support and metals were impregnated onto the wash coated supports. The activity of doped Rh catalysts was very high at low temperatures as compared to that of monometallic Rh catalysts. The catalyst doped with Ni and Ce was tested for stability for 50 h and no deactivation was found for this catalyst during this period.

Casanovas et al. [72] used a two sided microchannel plate, one side with reforming catalyst and the other side with combustion catalyst, to produce hydrogen from ethanol in auto-thermal mode. In this study four different methods were used for preparing coated plates, such as wash coating, in situ co-precipitation, in situ urea-assisted precipitation and sol–gel. In situ urea-assisted precipitation was found to be better among the four methods used, in terms of adherence and final catalyst loading. Efficiency of the microreactor was calculated to be 71% using the formula $\eta = 100 \times$ mol of H_2/(mol of ethanol $\times$ 6 $\times$ 0.858), where, the factor 0.858 arises due to the fact that 14.2% of the total ethanol will be consumed in combustion reaction. Differences in both microstructure of catalyst

coatings and catalytic behavior were not observed even after exposure to thermal cycling for 24 h between 298 and 773 K.

Casanovas et al. [73] used three different types of catalytic wall reactors, viz. conventional monoliths [36], microchannels [72] and micro-monoliths [74] for SRE at low temperature. CoO_3 catalyst coated reactors were prepared by in situ thermal decomposition of cobalt hydroxide salts. Significant difference in activity was observed among the three reactors studied. Micro-monoliths preformed better than the other two reactors. The performance decreased as size of the channel increased.

Wang et al. [75] fabricated ceramic micro-components by "deep X-ray lithography and lost-mold" technology with dimensions 300 μm width, 400 μm height and 20 mm length. The components so fabricated were tested for SRE with 300 nm Ni film-catalysts, coated through sputtering process. The results from this study revealed that, the sputtered catalyst show better performance even at lower temperatures.

5.3. CO cleanup step

Effluent from ethanol reformer typically contains more than 10% CO. In many applications it is desirable to reduce the CO content to ppm levels, for example, in PEM fuel cell applications. Two routes have been suggested in the literature: (i) membrane separation and (ii) WGS followed by selective methanation of CO or PrOX.

5.3.1. Membrane route

In the case of membrane reactor, the process is very simple and Pd membranes are highly selective for H_2 permeation and possess excellent mechanical characteristics. A low hydrogen recovery (∼70% gas processed), requirement of high pressures on the reformer side, low pressure on the other side, failure at high temperatures, prohibitively high cost, etc. are the primary limitations of this process [31]. To increase the overall productivity of H_2 using membranes, integrated WGS with a H_2 gas separator, by preparing a composite membrane with four layers viz. Cu, aluminum, Spin on glass (SOG), and palladium, has been proposed [76]. Out of these layers, Cu acts as a WGS catalyst and Pd separates the H_2 from the other gases. Also, aluminum and palladium serves to increase the mechanical strength.

A micro-membrane with 66 nm Cu, 200 nm Al, 500 nm SOG, and 200 nm Pd withstood a maximum ΔP of 1 atm before failure. It was claimed that due to the nano-thin layer of Pd, the activation energy for hydrogen flux was decreased.

5.3.2. Chemical route

Water gas shift followed by preferential methanation or oxidation is widely studied for CO cleanup.

(i) Water gas shift reaction

In WGS, the steam reacts with water to give CO_2 and H_2 as follows:

$$CO + H_2O \leftrightarrow CO_2 + H_2, \quad \Delta H_{298} = -41\ \mathrm{kJ/mol} \tag{8}$$

For which the equilibrium constant is given by:

$$K_{eq} = \exp\left[\left(\frac{4577.8}{T}\right) - 4.33\right] \tag{9}$$

where T is in Kelvin

By this reaction, the CO content can be reduced from 10% to about 1%. WGS is mildly exothermic so the conversion of CO is thermodynamically controlled at high temperature; moreover the rates are very low at low temperature. Therefore, for every composition there will be an optimum temperature at which space-time yield is the highest. Two reactors are used to maximize the conversion: one at high temperature (HT-WGS) for achieving high rates and the other at low temperature (LT-WGS) to achieve high equilibrium conversion. Noble metal catalysts have reasonable activity even at low temperature and, with such catalysts; one can achieve high conversions in a single reactor, by maintaining a decreasing temperature profile along the reactor length.

Tonkovich et al. [77] have applied micro-reactor technology to exploit fast intrinsic kinetics on 5% Ru/ZrO_2 catalyst and found that, with this technology, the fuel processor size can be one or two orders less than that of conventional processes. Kolb et al. [78] employed microchannel reactors to screen and optimize the catalysts for WGS reaction. They tested a range of bimetallic catalysts ($Pt/CeO_2/Al_2O_3$, $Pt/Rh/CeO_2/Al_2O_3$) and $Pt/CeO_2/Al_2O_3$ was identified as the best candidate concerning selectivity and activity. The optimum platinum content was found to range between 3 and 5 wt.%, whereas the optimum ceria content ranged between 12 and 24 wt.%.

In a later work, the same group [79], integrated WGS with PrOX, using the same catalyst as developed for WGS. With this integrated reactor and with steam/carbon ratio of 3.3 and O_2/carbon ratio of 0.67, the iso-octane fuel was auto-thermally reformed completely, with CO content less than 50 ppm.

TeGrotenhuis et al. [80] developed a model for calculate the optimum temperature profile to maximize the conversion in WGS, and compared this with an optimized two reactor system with inter-stage heat removal. The catalyst required for the latter system was 2.5 times more than that for the former system, to achieve a conversion level of 93%.

Baier and Kolb [81] applied a simple one dimensional model to compare two configurations for WGS (a) combination of reactor/heat exchanger and (b) two stage reactor with intermediate water injection. The length required for configuration (a) was found to be 30% less than that required for configuration (b).

(ii) CO preferential oxidation (PrOX)

In WGS reaction, it is difficult to achieve a CO concentration below 1%, because of thermodynamic constraint on equilibrium conversion. So, generally PrOX is used to reduce the CO concentration below 50 ppm, which is the tolerance level of PEMFC. For PrOX reaction, the exit gases from the WGS reactor are mixed with the required amount of O_2 and passed over the PrOX catalyst. The main reactions that may take place are:

$$CO(g) + 0.5O_2(g) \rightarrow CO_2(g): \quad \Delta H_{298} = -283\ \mathrm{kJ/mol} \tag{10}$$

$$H_2(g) + 0.5O_2(g) \rightarrow H_2O(g): \quad \Delta H_{298} = -241.8\ \mathrm{kJ/mol} \tag{11}$$

If the oxygen content is not sufficiently high then there may be chances of reverse WGS, as follows:

$$H_2 + CO_2 \leftrightarrow H_2O + CO: \quad \Delta H_{298} = 41\ \mathrm{kJ/mol} \tag{12}$$

In a PrOX reactor, CO has to be oxidized preferentially in the presence of high concentration of H_2 and other hydrocarbon products. Hence, highly selective catalysts are required to maximize the CO conversion and minimize the conversion of H_2. Moreover, at PrOX conditions, methanation of CO and CO_2 is also promoted by some catalysts which will reduce H_2 productivity. Therefore, for PrOX reaction, catalyst selection is very important. The catalyst development for CO PrOX in packed bed reactors has been reviewed recently [82]. Whatever may be the catalyst, because of the lower rates at low temperature and lower selectivity towards CO PrOX at high temperature [83], the temperature window for highest CO PrOX is limited and is less than 50 °C. Moreover, the reaction is highly exothermic, so it is very difficult to maintain a constant temperature, which is essential for high activity of PrOX catalyst. In this context

micro-reactors perform well. Several studies have been done to test the feasibility of using micro-reactors for PrOX [3,83–85].

Gracia et al. [86] selected catalysts for ProX with the hypothesis that a catalyst which promotes CO adsorption and reaction at low temperature would be a good catalyst. Accordingly, two families of catalysts were developed, and Pt/Al_2O_3 doped with CeO_2 was found to be best catalyst for PrOX at temperatures below 90 °C.

Delsman et al. [87] designed an integrated heat exchanger/reactor for PrOX using a 3D CFD simulation for flow patterns, 2D heat transfer model and finally 1D model was used to simulate the integrated device. In their integrated device, one high temperature heat exchanger, one low temperature heat exchanger and PrOX reactor were integrated. With such a device, CO concentration can be reduced to 10 ppm while recovering heat with 90% efficiency.

Chen et al. [88] conducted PrOX reaction in a microchannel reactor and compared the reactor performance with that of a monolithic reactor (MR). The smaller dimensions of MR resulted in high heat mass transport, which in turn, resulted in higher reaction rates even at low contact times of 4–6 ms. Srinivas et al. [89] compared the performance of a Si micro-reactor with a packed bed micro-reactor by taking PrOX as a model reaction. They claimed that, wall coated micro-reactors do not suffer from any external mass transfer resistance.

Cominos et al. [90] screened several noble metal-based catalysts and their bimetallic combinations for PrOX, and found Pt–Ru/γ-Al_2O_3, Rh/Al_2O_3, Pt–Rh/γ-Al_2O_3 to be the most active and Pt–Rh/γ-Al_2O_3 to be the most stable catalyst.

6. Summary and conclusions

In the foreseeable future, the need for distributed power supply systems will be equally strong as that of large centralized systems; this is especially true for emerging economies and developing nations. Small scale hydrogen-based fuel cell systems will necessitate in-situ reforming of fuel, till the time large networks of hydrogen distribution systems penetrate the interior regions. Use of bio-generated ethanol presents a strong case as a potential renewable fuel for such small scale distributed applications. The synthesis of a microscale fuel processor for in-situ reforming requires the harmonization of technologies ranging from microfabrication, microscale boiling heat transfer and catalytic conversion, so that pure hydrogen, suitable for polymeric fuel cells, can be safely produced.

As regards the fuel pre-heater design, attention needs to be focused on the generation of fundamental transport data for flow boiling of ethanol–water mixtures in mini–microchannels. While data on flow boiling of mixtures in conventional sized channels is now available (although most studies are confined to flow of refrigerant mixtures), very few studies are reported in open literature on flow boiling of binary mixtures in mini/microchannels. The existing binary mixture studies in mini/microchannels are mainly limited to methanol–water mixtures. Experimental work with wide range of concentration ratio/composition must be done to verify the known correlations and to improve existing ones. Here, the determination of precise thermo-physical properties of ethanol–water mixture cannot be over emphasized.

As regards the fuel reformer, even though a large number of catalysts have been developed, the commercialization of this process requires more favorable catalysts, which can reduce the required reaction temperature and there by, the catalyst deactivation. Double layer catalyst system, with a careful selection of catalyst, can be a potential solution for this problem. Micro-reactor configuration is quite favorable for the implementation of double layer catalyst deposition scheme. Moreover, micro-devices can also be effectively used for heat integration.

For WGS reaction, the required temperature profile can be maintained in micro-reactor systems. Even though the PrOX reactions are highly exothermic, the small temperature window (~50 °C), required for high activity of PrOX catalyst, can be maintained in micro-reactors, through efficient heat exchange. Various micro-devices required for efficient generation of H_2 from ethanol, with very low concentration of CO, can be integrated with efficient heat recovery within the system, using micro-reactor technology.

In this paper we have tried to highlight the salient requirements and state-of-the-art for the development of the system for distributed hydrogen production system from bio-ethanol steam reforming. It is clear that considerable amount of work needs to be done in this important area of contemporary and long term interest.

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